

***In situ* Raman spectroscopic investigation of the structure and speciation of aqueous zinc bromide solutions to 500°C and 0.9 GPa**

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A Raman spectral study was carried out on three aqueous solutions of varying concentration and bromide/zinc ratio. Spectra were collected at 11 different temperature-pressure conditions ranging from ambient to 500 °C and up to 0.9 GPa. Raman band assignments for aqueous zinc bromide complex species reported in previous studies were used to determine the relative concentrations of ZnBr_4^{2-} , ZnBr_3^- , ZnBr_2 , and ZnBr^+ species at various temperatures and pressures. Our results are in close agreement with X-ray absorption spectroscopic (XAS) data [1], and confirm that the tetrabromo zinc complex, ZnBr_4^{2-} , is the predominant species up to 500 °C in solutions having high zinc concentrations (1 *m*) and high bromide/zinc molar ratios ($[\text{Br}]/[\text{Zn}] = 8$). This result is consistent with the observed predominance of the ZnCl_4^{2-} complex in chloride-rich fluid inclusion brines at high temperatures [2]. In agreement with previous Raman spectroscopic experiments [3], our measurements also indicate that species with a lower number of halide ligands and charge are favored with increasing temperature in dilute solutions, and solutions with low bromine/zinc ratios ($[\text{Br}]/[\text{Zn}] < 2.5$). The Raman technique provides an independent experimental means of evaluating the quality of XAS data obtained from high temperature disordered systems, and the combination of these two techniques provides complementary data on speciation and the structure of zinc (II) bromide complexes.

[1] Mayanovic *et al.* (2001) *Chem. Phys. Lett.* **336**, 212-218.

[2] Anderson *et al.* (1998) *Can. Mineral.* **36**, 511-524.

[3] Yang *et al.* (1988) *J. Sol. Chem* **17**, 751-762.

H₂O and Cl in basalts from Lau back-arc basin

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The subduction influence (fluid mobile elements) in basalts along the back arc Eastern Lau Spreading Center (ELSC) increases in several sharp gradients as the distance to the Tofua volcanic arc diminishes from 100 km in the north (19°S) to 40 km in the south (23°S). The six tectonic segments of ELSC display mixing relationships in trace element and isotopic ratios in which one end member is a subduction component that is distinctive for each segment. Basalts from the three well-sampled northern segments (ELSC-1, -2, and -3, from 19.2-20.7°S) are best for the study of volatiles because most did not lose H₂O by degassing, and because they display a wide range of H₂O/ element values on a local scale: from MORB-like to much higher values.

ELSC-1 has distinct trends of H₂O vs. Cl and of H₂O vs. Ba or Cl vs. Ba compared to ELSC-2. It is likely that higher Cl/H₂O and Cl/Ba along ELSC-1 are not caused by crustal assimilation but are primary mantle characteristics because 1) there is no correlation of Cl/Ba or Cl/H₂O with MgO; 2) no axial magma chamber has been detected seismically; 3) there is a good correlation of Cl with H₂O that extends to adjacent seamounts. However, a few samples have much higher Cl/H₂O, suggesting assimilation occurs sporadically here.

The correspondence of tectonic segmentation with volatile ratios is consistent with volatiles being supplied to each segment by separate hydrous diapirs that get their distinctive H₂O/Cl from the part of the slab from which they are initiated. Trends for each segment are generated by mixing between diapiric melts and melts from depleted, upwelling MORB-like mantle. Alternatively, geochemical segmentation might reflect focused magma supply to each segment from a distinctive heterogeneous source with redistribution of magmas along axis at crustal levels. The coherence of H₂O/Cl with segmentation despite rapid along-axis mantle flow beneath ELSC [1] suggests volatiles are transferred quickly from slab to surface. Large along-axis differences in H₂O output of the arc+back-arc suggests that H₂O is not removed with equal efficiency along-axis and that some H₂O may be retained in the wedge or in the slab.

[1] Conder & Wiens (2007) *EPSL* **264**, 299-307.